# II.I.1 Technoeconomic Boundary Analysis of Photobiological Hydrogen Producing Systems

Brian D. James (Primary Contact), George Baum, Kevin Baum, Julie Perez Directed Technologies, Inc. (DTI) 3601 Wilson Blvd., Suite 650 Arlington, VA 22201 Phone: (703) 778-7114; Fax: (703) 243-2724 E-mail: Brian\_James@directedtechnologies.com

DOE Technology Development Manager: Roxanne Garland Phone: (202) 586-7260; Fax: (202) 586-2373 E-mail: Roxanne.Garland@ee.doe.gov

Contract Number: NREL Subcontract No. AFH-8-88601-01

Subcontractor: Chuck Dismukes, Princeton, NJ

Project Start Date: April 15, 2008 Project End Date: August 31, 2009

## **Objectives**

- Develop conceptual system designs for photobiological, dark fermentation and microbial electrolysis hydrogen production systems.
- Leverage strengths of each production method to create integrated hydrogen producing systems that improve upon individual systems.
- Calculate capital costs, operating costs and feedstock costs for conceptual systems.
- Compute levelized hydrogen costs for conceptual design.
- Determine key factors affecting cost estimates.

## **Technical Barriers**

This project addresses the following technical barriers from the Hydrogen Production section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

(AK/AQ) Diurnal Operation Limitations

- (AJ/AP) Systems Engineering
- (AS) Waste Acid Accumulation

## **Technical Targets**

This project is conducting systems engineering analysis for biological hydrogen  $(H_2)$  production. These studies and their results support the accomplishment of Hydrogen Production section milestones from the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan, namely:

- Milestone 45: Projected hydrogen production cost of less than \$4/kg for photolytic hydrogen production.
- Milestone 46: Projected durability of 5,000 hours and cost of hydrogen of \$50/gge.
- Milestone 54: Projected hydrogen production cost of less than \$4/kg for photosynthetic bacterial hydrogen production.
- Milestone 57: Projected hydrogen production cost of less than \$4/kg for dark fermentative hydrogen production.

## Accomplishments

- Developed conceptual designs of biological hydrogen plants with sufficient detail to estimate hydrogen costs from such systems and compare on an equal basis those costs to other production costs from other methods.
- Hydrogen from the most cost-effective standalone system is approximately \$2.99/kg.
- Explored synergies between various biological hydrogen production methods to design and evaluate integrated systems.
- Hydrogen from the most cost-effective integrated system is \$3.21/kg.
- Concluded that the primary factor affecting hydrogen costs from these systems is plant size.
- Concluded that only in the systems utilizing acetic acid are nutrients a substantial cost.

 $\diamond \quad \diamond \quad \diamond \quad \diamond \quad \diamond$ 

## Introduction

This project considered multiple pathways for the biological production of gaseous hydrogen, including photobiological  $H_2$  production from a variety of genetically engineered algae and bacteria, dark fermentation of waste photobiological organisms, dark fermentation of lignocellulosic biomass, and the microbial electrolysis of fermentative waste. Additionally, the integration of multiple systems was considered for added hydrogen production and reduced cost. Within the analysis, five different photobiological organisms, three different fermentative pathways, and three different integrations of these systems were examined. Those organisms and systems are described in Table 1.

TABLE 1.	Organisms	and Systems	Analyzed
----------	-----------	-------------	----------

Pathway	Description			
Ph	otobiological			
B-1	A truncated antennae Chlamydomonas mutant with an oxygen-tolerant hydrogenase			
В-2	A truncated antennae Cyanobacteria mutant with an oxygen-tolerant hydrogenase			
В-3	A sulfate-permease Chlamydomonas mutant with a truncated antennae			
B-4	An immobilized, sulfur-deprived Chlamydomonas mutant with a truncated antennae			
B-5	A truncated antennae Purple Non- Sulfur (PNS) photosynthetic bacterial mutant			
Fermentative				
C-1, C-2, C-5	H <sub>2</sub> production using dark fermentation of photobiological systems algal waste			
Lignocellulosic Fermentation	H <sub>2</sub> production using dark fermentation of lignocellulosic feedstock (corn stover)			
MEC	H <sub>2</sub> production from a Microbial Electrolysis Cell (MEC) using fermentation waste as a feedstock.			
Integrated				
Stacked Beds (B-3/B-5)	Integration of Chlamydomonas and PNS photobiological systems for added hydrogen production due to fuller use of the light spectrum.			
Photobio/ Fermentation (B-1/C-1, B-2/C-2, B-5/C-5)	Integration of photobiological systems with the fermentation of their waste			
Lignocellulosic-MEC	Integration of Lignocellulosic fermentation and MEC that consumes the fermentative waste of fermentation as the MEC feedstock			

# Approach

For each of the photobiological systems, hydrogen production characteristics were defined, individual reactors conceptually designed, and levelized hydrogen costs calculated. Concepts, biological parameters, and



FIGURE 1. Hydrogen Cost Variation with Plant Size

current experimental data were provided by the National Renewable Energy Laboratory (NREL) Biological Hydrogen Working Group. However, organism performance was based on the author's projection of future genetically modified organisms rather than current laboratory experimental measurements. The analysis was based on developing a large plant size from several smaller modules. Each module was sized for 1 tonne/day (TPD) H<sub>2</sub> production with large quantities of similar components within a single module. Additional capital cost reductions as a result of increased purchase quantities are not likely thus, capital costs of larger plants increase linearly. Labor is a large contributor to the final cost of the hydrogen produced. Figure 1 shows most of the cost benefit is gained in the initial increase in plant size. Thus, a 10 TPD plant size was chosen for cost analysis.

For each fermentative system, a plant design was selected, its capital cost and performance were estimated, and resulting levelized hydrogen cost computed. The design and performance of the waste algae fermentation plants was based upon research conducted by NREL on fermentative organisms [1-3], and corresponds to projections of future optimized performance. The design and performance of the microbial electrolysis cell (MEC) plant draws heavily from the concepts and laboratory work conducted at Penn State University [4-7]. The design of the lignocellulosic fermentation plant was based largely on a detailed NREL report analyzing the performance and cost of ethanol production from corn stover [8]. Fermentation for ethanol production and fermentation for hydrogen production share many characteristics. Consequently, the current project work product was greatly enhanced by making use of this analogous analysis.

For the integrated systems, different combinations of the biological  $H_2$  production pathways were examined. Costs associated with these integrations as compared to the individual systems were evaluated. Four systems that have sufficient synergies to make integration a possibility were chosen for analysis.

#### Results

Given the systems listed previously, the feasibility, performance, capital cost, and resultant  $\frac{1}{2}$  were evaluated for each stand-alone and integrated system. System hydrogen production costs are summarized in Table 2.

TABLE 2.	$H_2$	Production	Costs
----------	-------	------------	-------

System	kg H <sub>2</sub> /day	\$/kg
Photobiological H <sub>2</sub> Production		
B-1 - Algal O <sub>2</sub> -tolerant Hydrogenase	10,000	\$2.99
B-2 - Cyanobacterium O <sub>2</sub> -tolerant Hydrogenase	10,000	\$2.99
B-3 - Algal Sulfate Permease	10,000	\$4.17
B-4 - Immobilized Algal, Sulfur deprived	10,000	\$6.02
B-5 - PNS Bacteria	10,000	\$10.36
Fermentation of Waste Algae/Photobacteria		
C-1 and C-2 - Effluent from B-1 and B-2	7	\$172.73
C-5 - Effluent from B-5	19	\$66.17
Fermentation of Lignocellulose - No byproduct credit 37,181		\$4.33
Fermentation of Lignocellulose - \$0.12/kg value of byproduct	37,181	\$2.09
MEC - Microbial Electrolysis Cell - Acetic Acid Feedstock	88,055	\$12.43
Integrated Photobiological - B-3/B-5 Stacked	10,600	\$5.25
Integrated Photobiological/Fermentor		
B-1/B-2 & C-1/C-2 Integration	10,007	\$3.21
B-5 & C-5 Integration	10,019	\$11.04
Integrated Lignocellulosic Fermentor/MEC	125,266	\$6.61

For the pure photobiological systems, B-1 and B-2 achieved the lowest costs, however, these results are predicated on major improvements in organism mutations achieving truncated antenna reductions, elimination of cell light saturation due to electron transfer rate limits, and successful operation of the reactor bed design. The B-3 and B-4 system costs are slightly higher and the systems are more complex, but the components have been more completely demonstrated. The B-5 system has the highest cost of the photobiological systems due the higher number of photons needed (11 to 15 vs. 4) to generate each  $H_2$ molecule and the high cost of the acetic acid feedstock. A sample of the plant design of a photobiological plant is shown in Figure 2.

The algae/bacteria fermentation systems have high costs due to the low organism feedstock input resulting in low  $H_2$  output. A large part of the resulting  $H_2$  cost is due to the labor (94-96% of total cost) since it is analyzed as a stand-alone system. The cost contribution of the labor drops drastically when integrated with a photobiological system. The results are based on a projected fermentation output of highly sulfurdeprived organisms and do not fully exploit the organic components of the algae feedstock. It is expected that future bacteria and processing developments could facilitate more extensive conversion of the starch, lipid and protein content of the algae into  $H_2$ .

The lignocellulosic fermentation achieved a moderately low  $\rm H_2$  cost, using bacteria and processing that has been proven in lab environments, but not in large scale demonstrations. There is also a high potential for cost reduction from the sale of the 51% acetic acid content liquid byproduct. If the byproduct had a market value of \$0.12/kg (as compared to the market price of ~\$0.60/kg for acetic acid [9]), the net  $\rm H_2$  cost would be reduced to nearly \$2.00/kg.

For the MEC system, the moderately high  $H_2$  cost resulted from the very dilute acetic acid/water reactant, and necessitated a very large reactor volume and correspondingly very large anode and cathode areas. This high capital cost was coupled with high acetate market price, which could potentially be reduced by lowering acetic acid purity, which is not marketed, but is available as a fermentor byproduct. The immaturity of the full-scale system concepts and components indicated that there is extensive potential for future cost reductions. Cost saving could also arise from higher concentration of electrolyte and higher pressure operation.

For the integrated, stacked photobiological system, the  $H_2$  cost is between the cost of the two individual stand-alone systems. For the integrated photobiological algae/fermentor system, the  $H_2$  costs are higher than the stand-alone photobiological system. For the integrated fermentor/MEC system, the MEC's  $H_2$  production cost is reduced significantly due to the free feedstock. However, due to high MEC capital costs, the cost of the combined system is still significantly higher than the fermentor alone. In all of these systems there is no cost benefit to integration.

#### **Conclusions and Future Directions**

The analysis portion of this project was completed at DTI during the  $2^{nd}$  quarter of 2009. Incorporation of comments to the final report remains. Although the knowledge gained from this analysis was of great



FIGURE 2. B-1 Plant Design

benefit, further studies are recommended to improve the understanding of how these systems can contribute to the hydrogen transition.

- Future Photobiological Systems analyses recommended are:
  - Validation of future performance projections with experimental data.
  - System evaluation using alternative reactor bed concepts.
  - Analysis of a B-4 system with an alternative immobilization mat, made of alginate, which can be used as fermentor feedstock so these two systems can be integrated.
- Future Algae Fermentation Systems analyses recommended are:
  - Evaluation of pre-treatment processes to significantly increase the algae-to-hydrogen conversion rate.
  - Modification of algae feedstock characteristics so that it is better suited for fermentation.

- Reduction in fermentation process duration to assess impact on costs.
- Future Lignocellulose Fermentation Systems analyses recommended are:
  - Verification of byproduct market demands, prices and supply to validate H<sub>2</sub> production costs.
  - Detailed design of byproduct component separation (acids, ethanol, etc.).
- Future MEC Systems analyses recommended are:
  - Optimization of process and components for low capital cost systems.
  - Correlation of ion transport loss to reactor size.
- Future Integrated Systems analyses recommended are:
  - Exploration of additional combinations to achieve reduced hydrogen cost.
  - Modification of reactor bed configurations for the purpose of improving the integrated system costs.

## **FY 2009 Publications/Presentations**

**1.** Deliverable 4.4.3. Draft Final Report. Contract Milestone Report. 24 June 2009.

2. 2009 DOE Hydrogen Program Review - Washington, DCMay, 2009. Presentation PD# 15.

**3.** Deliverable 4.3.1. Task C Part II: Lignocellulosic Fermentative H<sub>2</sub> Production Subsystems Results & Discussion. Contract Milestone Report. 17 April 2009.

**4.** Deliverable 4.2.2. Task B: Photobiological H<sub>2</sub> Production Subsystems Combined Report, Characterization & Results. Contract Milestone Report. 23 January 2009.

**5.** Deliverable 4.2.1. Task B: Photobiological H<sub>2</sub> Production Subsystems Characterization Report. Contract Milestone Report. 24 December 2008.

## References

**1.** Benemann, John R. and Paola M. Pedroni. 4.3 Biological production of H2: mechanisms and processes.

**2.** Maria Ghirardi. Project 3.3:Photobiological systems for Hydrogen Photoproduction. 1<sup>st</sup> Quarter 2008 Report.

**3.** Kosourov, S.; Seibert, M.; Ghirardi, M. L. (2003). Effects of Extracellular pH on the Metabolic Pathways in Sulfur-Deprived H2-Producing Chlamydomonas Reinhardtii Cultures. Plant and Cell Physiology. Vol. 44(2), 2003; pp. 146-155; NREL Report No. JA-590-34437.

**4.** Call, Douglas and Logan, Bruce, "Hydrogen Production in a single Chamber Microbial Electrolysis Cell Lacking a Membrane." Environmental Scientific Technology 42 (2008): 3401-3406.

**5.** Logan, Bruce et al. "Microbial Electrolysis Cells for High Yield Hydrogen Gas Production from Organic Matter." Environmental Scientific Technology 42 (2008): 8630-8640.

**6.** Call, Douglas et al. "High Surface Area Stainless Steel Brushes as Cathodes in Microbial Electrolysis Cells." Environmental Scientific Technology (2008).

**7.** Logan, Bruce et al. "Graphite Fiber Brush Anodes for Increased Power Production in Air Cathode Microbial Fuel Cells." Environmental Scientific Technology (2007).

**8.** Aden A. et al. Lignocellulosic Biomass to Ethanol Process Design and Economics Utilizing Co-Current Dilute Acid Prehydrolysis and Enzymatic Hydrolysis for Corn Stover. NREL/TP-510-32438, June 2002.

**9.** Lee, Sang Y. "Plastic Bacteria? Progress and prospects for polyhydroxyalkanoate production in bacteria." Trends in Biotechnology Vol 14, pp. 431-438. 1996.